

*On Scandium.—Part II.*

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(Abstract.)

This is a continuation of the paper read in April, 1908,\* in which, after describing the mode of extracting Scandia from the mineral wiikite, the principal salts, 23 in number, were described, their formulæ and analytical results being given in detail.

Since that publication, G. Eberhard,† of the Astrophysical Observatory, Potsdam, reasoning from the fact that the strongest lines of the Scandium spectrum are observed in the spectra of stars in diverse stages of development, has come to the conclusion that Scandium must be universally distributed on the earth. Investigating the arc spectra of 366 minerals and rocks, he obtained the remarkable result that Scandium in small quantities is actually one of the most widely distributed earth elements.

These results of Eberhard were quickly verified by Prof. R. J. Meyer,‡ Berlin University, who, in a preliminary paper, has described experiments on extracting Scandia from the Zinnwald wolframite. Prof. Meyer concludes that this wolframite contains from 0·14 to 0·16 per cent. of rare earths, and that these earths contain 0·30 to 0·33 per cent. of Scandia. Thus the original wolframite would contain about  $0·15/100 \times 0·315/100 = 0·04725/10,000$  or about 0·0005 per cent. of Scandia.

On reading Prof. Meyer's paper I examined the felspar and mica which were associated with the parcels of wiikite procured by me from Finland. The felspar contains a small percentage of rare earths, but no trace of Scandia could I detect on examining their photographed spectra, the dominant line, wave-length 3613·984, being entirely absent. The mica was found to contain about 1 per cent. of rare earths, and in the photographed spectrum the dominant lines of Scandium are plainly visible. From a comparison of the spectra with those taken of the rare earths from wiikite I should estimate the Scandia at about half that in the earths of the best black wiikite.

\* 'Phil. Trans.,' vol. 209, pp. 15—46, March 4, 1908.

† 'Sitzungber. Kgl. Preuss. Akad. Wissensch.,' 1908, vol. 38, p. 851.

‡ 'Zeit. für Anorg. Chem.,' vol. 60, p. 134, November 17, 1908; and 'Chemical News,' vol. 99, pp. 85, 97, February, 1909.

A specimen of wolframite from Zinnwald was found to contain less than 1 per cent. of rare earths, and in the photographed spectrum of these earths the dominant lines of Scandium were strong, accompanied by only the faintest trace of yttrium or ytterbium lines.

In the quantitative determination of the Scandia in the salts described in the present paper the residual earth was collected from the mother-liquor and a photograph taken of its spectrum. A comparison of the pair of spectra shows at once if any separation has been effected between the earths present. When separation is apparent further experimentation on a larger scale is reserved to a future occasion.

*Scandium Iodate*,  $\text{Sc}(\text{IO}_3)_3 + 18\text{H}_2\text{O}$ , is prepared by the metathesis of a soluble Scandium salt with ammonium iodate. It forms a white crystalline powder almost insoluble in water.

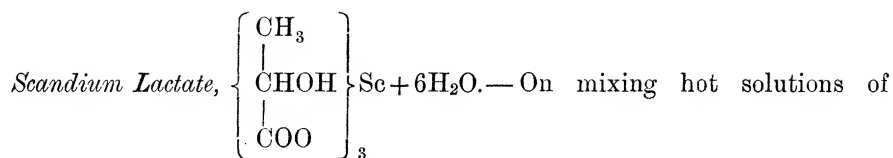
*Scandium Sulphite*,  $\text{Sc}_2(\text{SO}_3)_3$ , is a white insoluble powder formed by mixing a soluble Scandium salt with sodium sulphite. It is anhydrous and gradually decomposes on exposure to dry air.

*Scandium Borate*,  $\text{ScBO}_3$ , is a white powder, having the appearance under the microscope of minute transparent spheres. In transmitted polarised light each spherulite shines like a point of light on the dark field when the analyser is crossed, each point alternately disappearing and reappearing as the stage is rotated.

*Scandium Aurochloride*,  $3\text{ScCl}_3 \cdot 2\text{AuCl}_3 \cdot 21\text{H}_2\text{O}$ , is prepared by mixing strong solutions of the component chlorides, and allowing the mixture to evaporate slowly over sulphuric acid in a vacuum desiccator. The double salt separates out in a felt-like mass of needle-shaped crystals of a yellow colour and very deliquescent.

*Scandium Platinocyanide*,  $\text{Sc}_2[\text{Pt}(\text{CN})_4]_3 + 21\text{H}_2\text{O}$ , is formed by the metathesis in the cold of Scandium sulphate and barium platinocyanide. It crystallises out in large monoclinic prisms on a rhombic base, the angles of which are  $81^\circ 20'$  and  $98^\circ 40'$ . They are very soluble in water, and are insoluble or nearly so in absolute alcohol, and frequently group themselves in rosettes. They are dichroic, crimson by transmitted light, and a rich metallic green by reflected light. The reflected and transmitted rays are oppositely polarised.

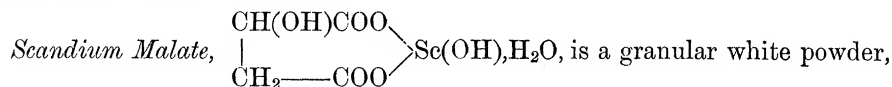
*Scandium Mono-chloroacetate*,  $(\text{CH}_2\text{ClCOO})_2\text{ScOH} + 2\text{H}_2\text{O}$ .—Scandium hydroxide, ground and well shaken with a cold aqueous solution of mono-chloroacetic acid, dissolves slowly and almost completely. The clear filtered solution, evaporated in the cold over sulphuric acid, deposits a crystalline crust, appearing under the microscope as flower-like groups of stellate crystals, and showing good colour when examined by polarised light.



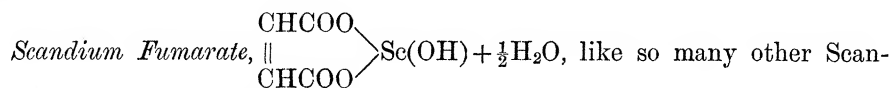
Scandium nitrate and ammonium lactate, the Scandium salt on cooling separates in white feathery crystals, slightly soluble in cold, more soluble in hot water, and easily soluble in ammonia.

*Scandium Malonate*,  $\text{CH}_2 \begin{array}{c} \diagup \text{COO} \\ \diagdown \text{COO} \end{array} \text{Sc}(\text{OH})$ .—Scandium hydroxide dissolves readily in a cold aqueous solution of malonic acid, and the solution when heated deposits a semi-transparent granular precipitate, having no crystalline appearance under the microscope. This precipitate partially dissolves on cooling.

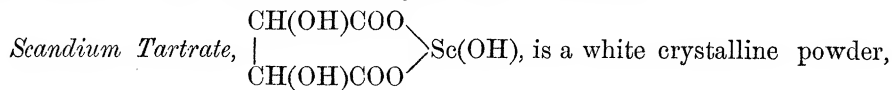
If this solution is boiled for some time a dense precipitate is formed, which on cooling does not re-dissolve.



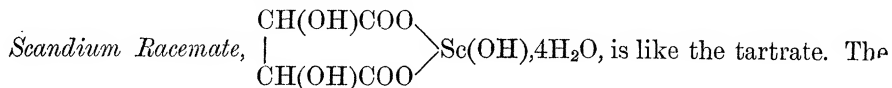
soluble in hot and difficultly soluble in cold water. It is easily soluble in ammonia, and is not precipitated from the ammoniacal solution by dilute acetic or malic acid.



dium salts, is more soluble in cold than in hot water. It is a white powder, appearing under the microscope as very minute spheres, slightly soluble in hot, more so in cold water, and easily soluble in ammonia.



insoluble in hot, slightly soluble in cold water, and insoluble in alcohol. Dried in a desiccator it is anhydrous.



two salts, however, are not quite similar. The racemate comes down less plentifully on boiling, and it is not anhydrous as is the tartrate, but contains four molecules of water, one of which is driven off at 115°.

Equal weights of tartaric and racemic acids were dissolved in separate bottles of water, and equal quantities of Scandium hydroxide added to each bottle, the amount being chosen so that all dissolved except a small quantity.

The two bottles were shaken in the cold for half an hour and filtered. The clear solutions were well boiled. A precipitate was formed in each, but that in the tartrate was double that in the racemate.

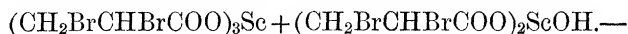
*Scandium Lævo-tartrate*,  $\begin{array}{c} \text{CH(OH)COO} \\ | \\ \text{CH(OH)COO} \end{array} \text{Sc(OH),2H}_2\text{O}$ , is prepared in a

similar way to the tartrate. Dried in a desiccator over sulphuric acid it contains one molecule of water. Dried in the air it contains two molecules of water.

*Scandium Meso-tartrate*,  $\begin{array}{c} \text{CH(OH)COO} \\ | \\ \text{CH(OH)COO} \end{array} \text{Sc(OH),H}_2\text{O}$ , is prepared by

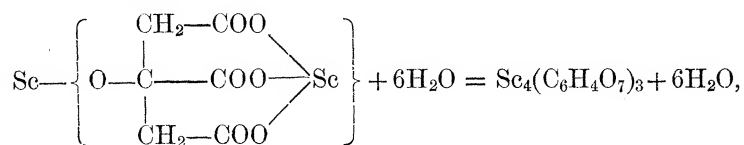
gently warming a slight excess of Scandium hydroxide with aqueous meso-tartaric acid and then boiling the filtered solution. The meso-tartrate comes down as a white granular precipitate. It is well washed with boiling water and dried over sulphuric acid in a desiccator for twenty-four hours. In this state it contains one molecule of water.

*Scandium  $\alpha\beta$ -Dibromopropionate*,



I have not prepared either the normal or the basic dibromopropionate in a pure state, but I have obtained a salt corresponding to equimolecular proportions of the two salts, having the above composition. Scandium dibromopropionate is almost insoluble in hot or cold water, and when dried over sulphuric acid in a desiccator is a white amorphous powder, so extremely electrical that it requires great care in powdering and moving it from one vessel to another or it flies out of the mortar or watch-glasses.

*Scandium Citrate*,



is a dense white precipitate, soluble in excess of ammonium citrate solution.

*Scandium Orthochlorobenzoate*,  $\text{C}_6\text{H}_4\text{ClCOOScO} + (\text{C}_6\text{H}_4\text{ClCOO})_2\text{Sc(OH)}$ , forms a white amorphous precipitate, slightly soluble in hot water.

*Scandium Metanitrobenzoate*,  $[\text{C}_6\text{H}_4(\text{NO}_2)\text{COO}]_3\text{Sc} + 4\text{H}_2\text{O}$ .—Metanitrobenzoic acid is neutralised with ammonia, a hot solution of Scandium nitrate added till no more precipitate is formed, and the whole boiled for a few minutes. A white crystalline precipitate falls down. The metanitrobenzoate is very slightly soluble in water, and from a hot solution it separates in the form of flat crystals displaying brilliant colours when examined by polarised light.

The Scandia used in some of these experiments was intentionally not quite pure, being vitiated with a little yttria and ytterbia. On testing, the Scandia resulting from the decomposition of the metanitrobenzoate showed no trace of the dominant lines of yttrium or ytterbium, while the earth precipitated from the mother-liquors of the Scandium metanitrobenzoate on spectroscopic examination showed strong lines of both impurities. It will be remembered that Neish found that metanitrobenzoic acid was capable of separating thoria from its accompanying earths with quantitative accuracy. Further experiments with this acid are in progress.

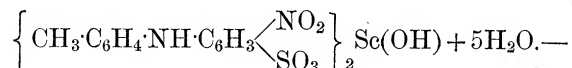
*Scandium Phthalate*,  $C_6H_4 \begin{smallmatrix} \diagup COO \\ \diagdown COO \end{smallmatrix} \rangle Sc(OH) + H_2O$ .—When a solution of

Scandium nitrate is added to a solution of ammonium phthalate, an amorphous white precipitate of Scandium phthalate comes down. It is slightly soluble in excess of Scandium nitrate, and insoluble in water or in excess of ammonium phthalate.

*Scandium Tetrachlorophthalate*,  $C_6Cl_4 \begin{smallmatrix} \diagup COO \\ \diagdown COO \end{smallmatrix} \rangle Sc(OH) + 6H_2O$ .—On mixing

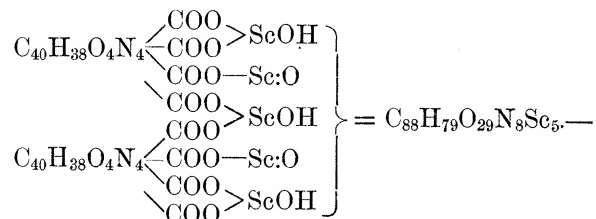
together equivalent proportions of Scandium nitrate and ammonium tetrachlorophthalate a dense white amorphous precipitate comes down, almost insoluble in hot or cold water. When washed and dried in the air, Scandium tetrachlorophthalate has the composition given above.

*Scandium 2-Nitrophenyl-4'-tolylamine-4-sulphonate*,



The sodium salt of this acid is dissolved in water and a solution added of Scandium nitrate. If the solutions are strong, a red precipitate falls; if weak, the mixture must be concentrated. On cooling, the Scandium salt separates in feathery crystals of a fine scarlet colour. It must be purified by re-crystallisation from a hot aqueous solution. The crystals are slightly soluble in cold water.

*Scandium Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylate*,



By the kindness of Dr. Silberrad I have had an opportunity of experimenting with octamethyltetraminodihydroxyparadixanthylbenzenetetra-carboxylic acid.

Previous experiments would lead one to expect the Scandium salt of this acid to have the composition  $C_{44}H_{40}O_{14}N_4Sc_2$ . This I could not prepare, the salt produced by metathesis containing more Scandium than this formula admits of. The only Scandium salt I could form of this acid has the composition shown above.

Octamethyltetraminodihydroxyparadixanthylbenzenetetra-carboxylic acid is a dark red powder, insoluble in water and easily soluble in dilute ammonia. The solution in ammonia, very slightly alkaline, is exactly neutralised with acetic acid; to the hot solution Scandium acetate is added and the whole boiled. On cooling, scandium octamethyltetraminodihydroxyparadixanthylbenzenetetra-carboxylate comes down as a red powder, insoluble in cold water.

More than once I have been asked why I chose such very out-of-the-way acids wherewith to prepare Scandium salts? I give my chief reason:—Attempts on several occasions have been made to discover a means of separating some of the “rare earths” from their companions by forming compounds with weak organic acids. Thus, in 1897, Kosmann\* employed citric acid in the separation of thoria. Urbain† used acetylacetate of sodium for the same purpose. Metzger‡ tried maleic acid, cinnamic acid, picric acid, phthalic acid, and fumaric acid. He found fumaric acid effectual in separating thoria from the other earths in monazite, while the other acids also gave partial separations, although not complete.

In 1904, Neish§ tried many organic acids for the separation of the rare earths, chiefly thoria. Among other acids, he tried gallic, tannic, citric, salicylic, oleic, linoleic, paratoluic, oxyisophthalic, benzoic, meta-, ortho-, and para-nitrobenzoic, and fumaric. Of these, metanitrobenzoic acid proved most effectual, the process being capable of accurate quantitative results. It was found that other rare earths besides thoria behaved differently towards these acids, but the variation was not sufficient to enable the reactions to be used for accurate separations.

Soon after those experimental papers appeared I commenced similar researches hoping to find an organic reagent which would be a precipitant for some of the yttria earths—if not with quantitative accuracy, at all events

\* ‘Chem. Centralb.,’ 1897, Part I., p. 837; ‘Chemical News.,’ vol. 86, p. 218.

† ‘Bull. Soc. Chim.,’ 1896, vol. 15, p. 347.

‡ ‘Journ. Am. Chem. Soc.,’ vol. 24, No. 10; ‘Chemical News.,’ vol. 86, pp. 218, 229, 242.

§ *Ibid.*, vol. 26, No. 7; ‘Chemical News.,’ vol. 90, pp. 196, 201.

with sufficient separation to allow a fractionation method to be based on the reaction. My results, not being sufficiently definite, were never published; but as the organic acids were in my laboratory when the Scandium research was commenced, I preferred to use these acids, of which the purity and the history were known, rather than start afresh with acids of unknown history.

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*On the Rotatory Character of some Terrestrial Magnetic Disturbances at Greenwich and on their Diurnal Distribution.*

By ROBERT B. SANGSTER.

(Communicated by Dr. C. Chree, F.R.S. Received March 8,—Read April 28, 1910.)

On the occasion of a brilliant display of aurora some apparently rotatory movements in the position of the corona suggested to the author the possible existence of similar changes of direction in the total magnetic force during disturbance. For investigating these changes the most convenient available data were the plates published with the "Greenwich Magnetical and Meteorological Observations" (hereafter referred to as the "Report"), showing on a reduced scale the diurnal registers of the three components of magnetic force for several disturbed days in each year. The eight years 1900–7 were dealt with, and a preliminary inspection of all the registers figured for these years was made to select an example for special consideration. The published registers are reduced in scale from the originals in the ratio 11 : 20, and to lessen the chance of error on this account, it was decided to select a disturbance showing comparatively slow, but steady and decided, changes. The registers selected in the first instance were those for October 12, 1903, and it was decided to determine the variation in direction of the total force from 18 hours onwards, at intervals of about 5 minutes, leaving out of account the effect of the small temperature variations recorded, for reasons presently to be stated. This variation in direction was found in terms of transverse deflecting force, the unit employed being  $1 \times 10^{-5}$  C.G.S. (1  $\gamma$ ).

In the following remarks the letters D, H, and Z denote the declination, the horizontal force, and the vertical force, respectively; F and I, respectively, denote the total force and the dip; while the prefix  $\Delta$  signifies inequality increments. Ordinates of the components D, H, and Z were measured on the plate at time intervals of 1/40 inch, corresponding to a measure once